



Vapor pressure and enthalpy of vaporization of oil of catnip by correlation gas chromatography



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ABSTRACT

The vaporization enthalpy and vapor pressure of the two nepetalactones found in *Nepeta cataria* have been evaluated by correlation gas chromatography. Vaporization enthalpies at $T = 298.15$ K of $\{(68.0 \pm 1.9)$ and $(69.4 \pm 1.9)\} \text{ kJ} \cdot \text{mol}^{-1}$ have been derived for the minor diastereomer, (4a*S*,7*S*,7a*S*)-nepetalactone, and major one, (4a*S*,7*S*,7a*R*)-nepetalactone, respectively. Vapor pressures also at $T = 298.15$ K of $p = (1.2 \pm 0.04)$ Pa and (0.91 ± 0.03) Pa have been evaluated for the minor and the major stereoisomer. In addition to being of interest because of the remarkable effect it has on various felids, oil of catnip is also quite effective in repelling mosquitoes, comparable to diethyl-*m*-toluamide (DEET). The vapor pressures evaluated in this work suggest that the two stereoisomers have similar volatility to DEET at ambient temperatures.

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1. Introduction

The essential oil from the plant, *Nepeta cataria*, has held the interest of many because of the remarkable effect it has on various felids. Best known as “Oil of Catnip”, the structure of this material has also provided a long term fascination to chemists. The structure of the major component of the essential oil isolated by steam distillation was elucidated in several reports by McElvain [1,2] and co-workers and by Meinwald [3] in the middle of the last century. The major component isolated was (4a*S*,7*S*,7a*R*)-nepetalactone. Some caryophyllene and a small amount of the (4a*S*,7*S*,7a*S*) diastereomer along with some other minor products have also been reported. Additional diastereomers of nepetalactone have more recently been isolated from related plants [4]. The structures and absolute configurations of (4a*S*,7*S*,7a*R*)-nepetalactone and the (4a*S*,7*S*,7a*S*) diastereomer are illustrated in figure 1 [5].

Several *Nepeta* species (Lamiaceae/Labiatae) are known to contain nepetalactones and the plants are found widespread throughout the world. They have been used extensively in folk medicine for treatment of a variety of respiratory, nervous and gastrointestinal disorders [6]. The essential oil as well as the two individual nepetalactones are also powerful insect repellants [6]. The activity against *Aedes aegypti* (yellow fever mosquito), has been found to be comparable to diethyl-*m*-toluamide (DEET) and the former exhibits better spatial repellency at the same concentration when

monitored in a controlled environment [7]. Similar activity in comparison to DEET has been reported against major Afro-tropical pathogen vector mosquitoes, such as *Anopheles gambiae* [8].

Correlation gas chromatography (CGC) is a technique that has been developed to complement existing methods for evaluating vaporization enthalpies and vapor pressures [9]. One of the distinct advantages of this technique is that it is capable of providing pure component properties on materials that are not readily available in high purity and/or in large (>100 mg) quantities. The quality of the vaporization enthalpy and vapor pressures evaluated depends on selection of appropriate standards and on the quality of the physical properties available. Prompted by our previous interests in the transport properties of insecticides and pesticides, we have evaluated both the vapor pressures and vaporization enthalpies of (4a*S*,7*S*,7a*R*)- and (4a*S*,7*S*,7a*S*) nepetalactone. The compounds chosen as standards for this study are several γ and δ -lactones evaluated previously by us and others. Their structures are shown in figure 2.

2. Experimental methods

2.1. Compounds and purity controls

Table 1 lists the compounds selected as standards. All are either five or six membered ring lactones. The table reports their supplier and both their stated mass fraction purity as provided and our analysis by gas chromatography. As noted above, purity is not an issue with CGC since the chromatography generally separates the

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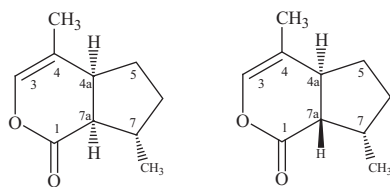


FIGURE 1. Structures of the major (1) and minor (2) diastereomers of (4aS,7S,7aR) and (4aS,7S,7aS)-nepetalactone isolated from *Nepeta cataria*, respectively.

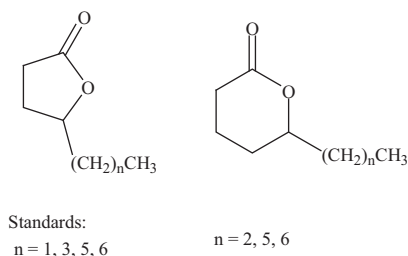


FIGURE 2. The structures of the γ and δ -lactone standards.

TABLE 1
Provenance and mass fraction purity of the materials used.

Compound	CAS registry no	Supplier	Mass fraction purity (supplier)	Mass fraction purity (GC)
γ -Hexanolactone	695-06-7	Bedoukian	>0.98	0.993
γ -Octanolactone	104-50-7	Bedoukian	>0.97	0.996
δ -Octanolactone	698-76-0	Bedoukian	0.98 ^a	0.989 ^{a,b}
γ -Decanolactone	706-14-9	Bedoukian	0.97	0.984
γ -Undecanolactone	104-67-6	SAFC	>0.98	0.984
δ -Undecanolactone	710-04-3	Bedoukian	0.98 ^a	0.948 ^{a,c}
γ -Dodecanolactone	2305-05-7	Bedoukian	0.97	0.930
δ -Dodecanolactone	713-95-1	Bedoukian	0.98 ^a	0.983 ^{a,d}
Nepetalactone isomers	490-10-8	Dr. Adorable, Inc. ^e	e-Bay	0.1:0.73:0.17 ^e

^a Sum of isomers, reference [5].

^b Two isomers: 0.977, 0.23; the minor isomer separated but was not identified.

^c Two isomers: 0.928, 0.072; the minor isomer separated but was not identified.

^d Two isomers: 0.985; 0.015; the minor isomer separated but was not identified.

^e Ratio of (4aS,7S,7aS)-nepetalactone: (4aS,7S,7aR)-nepetalactone: caryophyllene, respectively; additional details available in Sections 2.1, 2.3 and in the [supporting information](#).

impurities. Furthermore we have found that even when there is total retention time coincidence, the thermochemical properties evaluated for the co-eluters do not appear to be influenced significantly [10].

Catnip oil was purchased from Dr. Adorable Inc., available from e-Bay. The description of the material by the supplier was described as “Catnip, essential organic pure, *Nepeta cataria*, part flowering tops, steam distilled; Country of origin: Canada.” Analysis of the material by gas chromatography suggested the presence of a carrier which was confirmed by infrared analysis. The IR spectrum indicated the presence of a substantial hydroxyl stretch, suggestive of an alcohol or glycol. The catnip oil was therefore treated as follows: A portion of the material was added to water and extracted with methylene chloride. The methylene chloride extract was then washed with water several times and dried. The extract

was then analyzed by both gas chromatography and GCMS. Additional details are provided below and in the [supplemental data](#).

2.2. Methods

GC–MS analyses were carried out using a Hewlett Packard GC/MS System Model 5698A system operating in the EI mode at 70 eV, equipped with a Supelco SLBTM-5 MS capillary column (30 m \times 0.25 mm; 0.5 μ m film thickness) using He as the carrier at an oven temperature, $T = 289$ K. The mass spectra were compared with those available in the NIST/EPA/NIH MS library.

Gas chromatographic measurements were performed on an HP 5890 gas chromatograph running HP Chemstation. Isothermal chromatograms were obtained over a $T = 30$ K temperature range at intervals of $T = 5$ K on a Supelco 15 m, 0.32 mm, 1.0 μ m film thickness SPB-5 capillary column at a split ratio of approximately 100/1 using helium as the carrier. The column temperature was maintained to $T = \pm 0.1$ K by the instrument and monitored continuously using a Fluke digital thermometer. The solvent used was methylene chloride. The solvent also served as the non-retained reference at the temperatures of the experiments. A typical chromatogram of the nepetalactones combined with the standards is shown in [figure 3](#). Unless noted otherwise, compounds are arranged in order of their elution off the column.

Residence time on the column, the adjusted retention time t_a , was measured as the difference between the retention time of an analyte and that of the solvent which was not retained by the column at the experimental temperatures. The residence time is inversely proportional to the compound’s vapor pressure off the column. Plots of $\ln(t_o/t_a)$, where the reference time $t_o = 60$ s, against $1/T$ resulted in a linear relationship in which the absolute value of slope of the line is related to an enthalpy divided by the gas constant, $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. All correlation coefficients, $r^2 > 0.99$. The enthalpy measured by this procedure, $\Delta_{\text{trs}}H(T_m)$, is the enthalpy of vaporization of the compound from the column at the mean temperature T_m and is related to the vaporization enthalpy of the pure material by Eq. (1) where $\Delta_f^\ominus H_m(T_m)$ represents the vaporization enthalpy of the pure material, and $\Delta_{\text{intr}}H(T_m)$ represents the enthalpy of interaction of the analyte with the column [11].

$$\Delta_{\text{trs}}H(T_m) = \Delta_f^\ominus H_m(T_m) + \Delta_{\text{intr}}H(T_m) \quad (1)$$

A second correlation between $\Delta_{\text{trs}}H(T_m)$ and $\Delta_f^\ominus H_m(T)$ of the standards where usually $T = 298.15$ K is also found to be linear and the resulting analytical expression can be used to evaluate the vaporization enthalpy of the targets using their experimentally measured enthalpies of transfer, $\Delta_{\text{trs}}H(T_m)$. As noted above, the best results are obtained when the standards bracket the targets and are closely related to the targets with respect to the number and type of functional groups present. Functional groups in this context refer to those containing heteroatoms.

Vapor pressures can also be evaluated by a similar procedure. Correlation of $\ln(t_o/t_a)$ with $\ln(p/p^\ominus)$ where $p^\ominus = 101325$ Pa of appropriate standards also results in a linear relationship that can be used with values of $\ln(t_o/t_a)$ of the targets to evaluate their vapor pressure. Repeated as a function of temperature, this procedure can provide a vapor pressure vs temperature profile of the targets. The applicable temperature range of the equations of the standards used to evaluate vapor pressure frequently differs from the experimental temperature range of the GC experiments used to evaluate the slopes and intercepts of both the targets and standards. Consequently, the equations describing the derived vapor pressure vs temperature profile of the standards evaluated by correlation are also made available as a guide to how well the vapor pressures are reproduced by the correlations at all applicable temperatures

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